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Janner, A.M.; Jonkman, H.T.; Sawatzky, G.A

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# Second-harmonic generation spectroscopy: A technique for selectively probing excitons

A.-M. Janner,\* H. T. Jonkman, and G. A. Sawatzky

Laboratory of Solid State Physics, Materials Science Centre, University of Groningen, Nijenborgh 4,  
9747 AG Groningen, The Netherlands

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We show that second-harmonic generation (SHG) and sum-frequency generation (SFG) are selective tools for probing excitons. In SHG and SFG measurements performed on  $C_{60}$  and CuCl films we observe Frenkel and Wannier excitons, respectively. On the other hand, no second-harmonic (sum-frequency) intensity enhancement was observed at energies above the conductivity gap. This is in strong contrast to, for instance, one-photon and two-photon absorption experiments. The selectivity of SHG and SFG for excitons compared to interband transitions can be explained in terms of coherence of the respective excitation processes.

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## I. INTRODUCTION

Second-harmonic generation (SHG) is mostly known as a surface and an interface sensitive tool for materials which have inversion symmetry.<sup>1</sup> However, SHG can also be used as a powerful spectroscopic tool. For example, it is possible to observe linear optical (electric-dipole) forbidden transitions using SHG.<sup>2-5</sup> Despite that nonlinear optical spectroscopy is still not a very common technique, since the arrival of the optical parametric oscillator more papers are presenting frequency-dependent SHG spectra, revealing the strict selection rules and the selective power of this technique.<sup>3,6-8</sup>

In this paper we present second-harmonic and sum-frequency spectra from  $C_{60}$  films and CuCl films. For both materials the excitonic states and the conductivity gap are covered by the available frequency range. This allows us to investigate the different way in which these excitations appear in nonlinear optical SHG.

Solid  $C_{60}$  is an example of a molecular crystal, which exhibits semiconductor behavior in certain respects. One example clearly demonstrating this behavior is the Frenkel excitons found in  $C_{60}$ . These excitons propagate via a charge-transfer-mediated mechanism.<sup>6</sup>

The conductivity gap of solid  $C_{60}$  is about 2.3 eV, as was found by photoconductivity<sup>9</sup> and by combined photoelectron and inverse-photoelectron spectroscopy.<sup>10</sup> Well below the conductivity gap several Frenkel excitons are present. These originate from the lowest intramolecular excitations, i.e., from the highest occupied molecular orbital (HOMO), the singlet  $h_u$ , to the lowest unoccupied molecular orbital (LUMO), the singlet  $t_{1u}$ . Due to the Coulomb attraction between the electron and the hole, the HOMO-LUMO excitations are split into a multiplet of four states with  $^1T_{1g}$ ,  $^1T_{2g}$ ,  $^1G_g$ , and  $^1H_g$  symmetry, respectively (see also Fig. 3 in Ref. 6). Since the ground state is of  $^1A_g$  symmetry, all four Frenkel excitonic states are optically forbidden (electric-dipole forbidden). However, the  $^1T_{1g}$  state is allowed for magnetic-dipole transitions and the  $^1H_g$  state is allowed for electric-quadrupole transitions. These are, therefore, observable in a SHG experiment<sup>2,11,12</sup> as we will see below.

In contrast to the molecular behavior of  $C_{60}$ , CuCl is a semiconductor with ionic character. Hence its excitons are typically Wannier excitons, which are energetically much

closer to the conductivity gap. The valence band of CuCl is formed by a hybridization of the filled  $3s^23p^6$  noble-gas shell of  $Cl^-$  ions and the  $3d^{10}$  shell of  $Cu^+$  ions.<sup>13</sup> The conduction band of CuCl is predominantly formed by Cu  $4s$  orbitals. Coupling of the electrons in the lowest conduction band to holes in the highest valence bands gives rise to the edge excitons, the so-called  $Z_3$  and  $Z_{1,2}$  Wannier excitons.<sup>14,15</sup> The conductivity gap of CuCl is about 3.4 eV. Goldmann<sup>15</sup> and Saito *et al.*<sup>16</sup> deduced this value from the excitonic fine structure in their optical spectra. Fröhlich *et al.*<sup>17</sup> and Reimann *et al.*<sup>18</sup> found the same value for the conductivity gap of CuCl from their two-photon absorption measurements.

By measuring the SHG [or sum-frequency generation (SFG)] in the energy region containing the  $C_{60}$  and CuCl excitons and their conductivity gap, we observed a remarkable difference in the second-harmonic intensity at the exciton energies and at the conductivity gap.<sup>19</sup>

## II. EXPERIMENTAL SETUP

The main part of the experimental setup is a Nd:YAG (yttrium aluminum garnet) laser, which produces pulses of approximately 8 ns [full width at half maximum (FWHM)] at a wavelength of 1064 nm (1.17 eV) with a repetition rate of 10 Hz. The second and third harmonic of the Nd:YAG laser are used to pump a dye laser and an optical parametric oscillator (OPO), respectively. The pumping of the OPO and the dye laser can be done either separately or synchronously. The synchronous configuration was needed for the SFG experiments. All the measurements were performed in ultrahigh vacuum (UHV) (base pressure of about  $5 \times 10^{-10}$  mbar) with a fixed geometry (the angle of incidence is  $45^\circ$ ). A reference quartz crystal was used to correct for changing laser characteristics such as pulse-to-pulse amplitude fluctuations. For the temperature-dependent measurements a He-flow cryostat (Oxford, Ultrastat) was used (4–500 K).

We grew 250-nm-thick  $C_{60}$  films *in situ* by evaporating  $C_{60}$  (purity better than 99.99%) from a Knudsen cell onto a MgO substrate at UHV pressures below  $4 \times 10^{-9}$  mbar. The  $C_{60}$  data were taken using a  $m_{in}-p_{out}$  ( $m \rightarrow p$ ) polarization combination, where  $m$  denotes 50%  $p$ - and 50%  $s$ -polarized

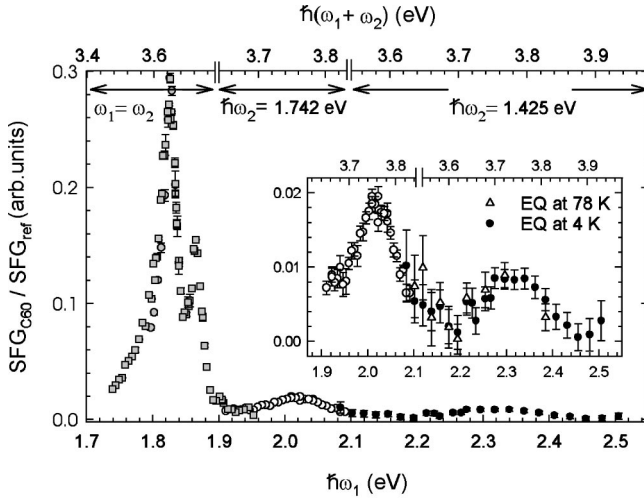


FIG. 1. Spectroscopic SHG (gray) and SFG (black and white) from  $C_{60}$  film. All these resonances are resonant at the fundamental  $\hbar\omega_1$  energy. For each experiment corresponding second-harmonic and sum-frequency energy is indicated in the upper  $x$  axis. At  $\hbar\omega_1 = 1.826$  eV there is the excitonic  $^1T_{1g}$  state (magnetic-dipole allowed). Due to mixing of this state with the (nearly) degenerate  $^1G_g$  state a second peak at 1.866 eV arises. We assign the resonance at 2.02 eV to the  $^1T_{1g}$  state coupled with the  $t_{1u}$  phonon mode, and the one at 2.3 eV to the excitonic  $^1H_g$  state [electric-quadrupole (EQ) allowed]. All the data are taken at  $T = 78$  K, except the black circles. However, the enlarged spectrum in the inset shows that there is no difference between the EQ data taken at 78 and at 4 K.

light. The CuCl film, 2.3  $\mu\text{m}$  thick, was grown by evaporating CuCl powder (purity of 99.995%) at 763 K on a MgO substrate. The film growth was done in a separate UHV chamber at a pressure of about  $1 \times 10^{-6}$  mbar. For all CuCl measurements we used the  $s_{in}-p_{out}$  ( $s \rightarrow p$ ) polarization combination.

### III. FRENKEL EXCITONS IN $C_{60}$

Figure 1 shows the combined spectroscopic SHG and SFG data from the  $C_{60}$  films taken at low temperatures. We observe four resonances within the available frequency range.

#### A. The resonances at 1.826, 1.86, and 2.02 eV

The first second-harmonic peaks at  $\hbar\omega = 1.826$  and  $\hbar\omega = 1.86$  eV were presented and discussed in previous papers.<sup>3,6,20</sup> Koopmans *et al.* demonstrated that the second-harmonic resonance at  $\hbar\omega = 1.826$  eV (Ref. 21) is due to a magnetic-dipole transition which is optically forbidden, and the transition was assigned to the  $^1T_{1g}$  Frenkel excitonic state.<sup>2,3</sup> The resonance at  $\hbar\omega = 1.86$  eV is only present below the rotational-ordering phase-transition temperature of 260 K.<sup>6</sup> We explained this by a *mixing* of the nearly degenerate  $^1T_{1g}$  and  $^1G_g$  free molecule states, which is only possible in the low-temperature phase.<sup>20</sup> Calculations done by Munn *et al.*<sup>22</sup> support our assignment of the low-temperature

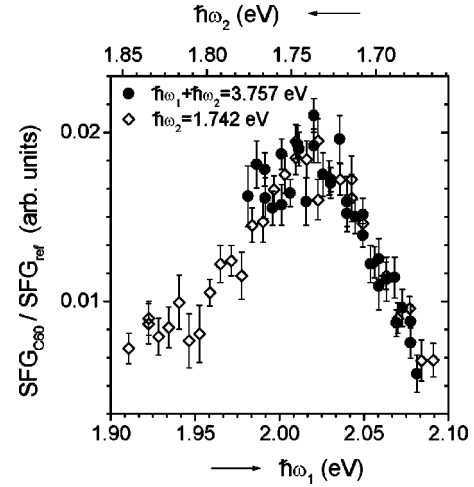


FIG. 2. The black dots are the SFG data obtained when the two laser frequencies  $\omega_1$  and  $\omega_2$  are scanned simultaneously so that  $\hbar\omega_1 + \hbar\omega_2$  is constant at 3.757 eV. Their agreement with the SFG data, where only one laser was scanned (white marks), proves that this resonance is resonant at 2.02 eV and not at 3.76 eV (see the two  $x$  axes in Fig. 1).

splitting in the  $C_{60}$  SHG spectrum to indirect interaction between Frenkel states, transmitted via the charge-transfer manifold.

The third nonlinear optical resonance in Fig. 1 is at about  $\hbar\omega_1 = 2.02$  eV. We observed this resonance in a SFG experiment, where the OPO was scanned from  $\hbar\omega_1 = 1.908$ – $2.102$  eV (590–650 nm), and the dye laser was fixed at  $\hbar\omega_2 = 1.742$  eV (712 nm). However, from this measurement alone it is not possible to determine whether the observed resonance is at  $\hbar\omega_1 = 2.02$  eV or at  $\hbar(\omega_1 + \omega_2) = 3.76$  eV. Therefore, we also scanned both lasers together, while keeping the sum frequency constant at 3.757 eV (330 nm). The result is plotted in Fig. 2 (closed circles). The sum-frequency intensity coincides nicely with the data obtained at fixed  $\hbar\omega_2$  and varying  $\hbar\omega_1$  (open diamonds). This clearly demonstrates that the resonance is at the fundamental frequency  $\omega_1$  and not at the sum frequency  $\omega_1 + \omega_2$ .

The resonance at  $\hbar\omega_1 = 2.02$  eV could only be observed in a SFG experiment in which the sum of the two laser frequencies was close to  $\sim 3.76$  eV, in other words, close to the  $2^1T_{1u}$  state (electric-dipole allowed). In a SHG experiment where the same  $\hbar\omega_1$  frequency range was used as in the SFG case no resonance was observed (Fig. 3). The SHG data were taken at room temperature. However, the temperature difference cannot explain the absence of the resonance, since a SFG measurement taken at room temperature also shows the (slightly shifted) resonance (see Fig. 3). This means that for our experiments it was necessary to be on double resonance in order to have sufficient sum-frequency intensity enhancement.

There are two possible origins for this resonance around 2 eV: (a) the electric-quadrupole-allowed  $^1H_g$  state or a charge-transfer excitonic state, or (b) the  $^1T_{1g}$  state coupled via the Herzberg-Teller mechanism with a vibrational mode. We first discuss case (a).

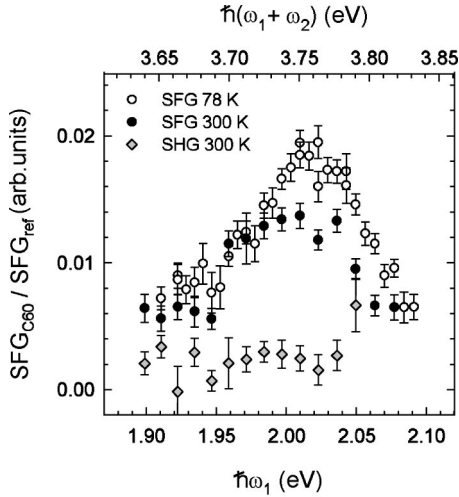


FIG. 3. The SFG resonance (circles) at about  $\hbar\omega_1 \approx 2.02$  eV was found at room temperature and at  $T = 78$  K while scanning  $\hbar\omega_1$  and keeping  $\hbar\omega_2$  fixed at 1.742 eV. The gray diamonds are the result of a SHG experiment, performed with the same  $\hbar\omega_1$  frequency range as input frequency. The SHG data do not show any resonance.

Assigning the 2.02-eV resonance to the  $^1H_g$  state (the highest energy state of the multiplet splitting) would yield a multiplet splitting of about 0.20 eV. This is much smaller than expected, since Negri *et al.*<sup>23</sup> calculated the multiplet splitting between the HOMO and LUMO states and found a splitting of about 0.35 eV. Furthermore, Shirley *et al.*<sup>24</sup> included electron-hole interactions in their *ab initio* calculations and found a multiplet splitting of 0.5–0.7 eV. Since the charge-transfer excitonic states are expected to lie above the  $^1H_g$  state,<sup>24</sup> they can also be excluded as candidates for the 2.02-eV resonance.

Case (b) seems more likely, and is supported by other experiments as well. Muccini *et al.*<sup>25</sup> claim from their optical-absorption measurements on single crystals of C<sub>60</sub> that the true origin of the  $^1T_{1g}$  state is at 1.86 eV. They observe a resonance at 2.03 eV as well, and assign this resonance to a  $^1A_g \rightarrow ^1T_{1g}$  transition induced by the  $t_{1u}$ -phonon mode with 0.179 eV (1440 cm<sup>-1</sup>) energy. This is in agreement with the quantum-chemical calculations of Negri *et al.*, which show that the most intense false origin in  $^1T_{1g}$  is  $\nu(t_{1u}) = 1437$  cm<sup>-1</sup> (0.178 eV).<sup>23</sup>

In our SHG experiment the true origin of the  $^1T_{1g}$  state at low temperature is not as clear as in Muccini's case, due to the mixing of the  $^1T_{1g}$  state with the  $^1G_g$  state. However, this problem can be solved by taking the first moment of the entire spectrum, which results in a mean frequency, i.e., a weighted average peak position. We determine the true origin of the  $^1T_{1g}$  state at 1.83 eV [see Fig. 2(b) of Ref. 6]. A vibronic coupling with the  $t_{1u}$  mode of 1437 cm<sup>-1</sup> would give rise to a peak at about 2.01 eV, in good agreement with our experimental observations.

An alternative explanation for the 2.02-eV peak was proposed by Kuhnke and co-workers.<sup>8</sup> They measured an optical SHG spectrum for C<sub>60</sub> using a fundamental energy range of 1.0 to 2.3 eV. Since they use a picosecond laser, which has a

much higher peak power than our nanosecond laser, they have an enhanced sensitivity to SHG. As a result, Kuhnke *et al.* do observe the resonance at 2.02 eV.<sup>8</sup> However, as noted before, in a SHG experiment it is not possible to distinguish whether the resonance is at  $\omega$  or at  $2\omega$ . Kuhnke *et al.* propose, that the transition at 2.02 eV is due to a double resonance with a transition at 4.04 eV and the vibrational structure of the  $^1T_{1g}$  state peaking at 2.02 eV.<sup>8</sup> However, from our SFG measurements (Fig. 2) we can clearly see that the resonance at 2.02 eV is at the fundamental frequency. Furthermore, the absence of a resonance in our SHG experiment does not support the existence of a transition at 4.04 eV.

Kuhnke *et al.* notice that the absorption spectra show a minimum at 4 eV, and they propose a  $2^1T_{1g}$  state as the possible origin for the 4.04-eV transition.<sup>8</sup> The main reason of Kuhnke *et al.* not to assign the 2.02-eV peak only to the  $^1T_{1g}$  state + phonon is that this transition is electric-dipole allowed. Since they observe at the fundamental energy 1.35 eV the electric-dipole transition between the HOMO and LUMO+1 (of 2.8 eV) and this peak is very weak, they argue that an electric-dipole transition would gain intensity only at the surface and not in the bulk. As a result, they conclude from the large second-harmonic intensity of the electric-dipole transition at  $\hbar\omega = 2.02$  eV that it needs to be doubly resonant. Based on the experimental data presented in this paper it is not surprising that a second-harmonic resonance from a state above the conductivity gap appears to be very weak. We will return to this point later. Here we would just like to state that Kuhnke *et al.* expect that the dipole (electric-dipole) contribution will be smaller than the quadrupole (electric-quadrupole and magnetic dipole) contribution, since the first originates from the surface and the later from the bulk. On the other hand, one might expect intuitively that the dipole process dominates over the quadrupole effects, since the atomic dimensions are much smaller than the wavelength of the light used.<sup>11,26</sup> Koopmans pointed out that these two ideas are counterbalanced, and that to first order the dipole and quadrupole processes can be of comparable importance.<sup>11</sup>

A striking difference between the SHG spectrum of Kuhnke *et al.*<sup>8</sup> and our spectrum (Fig. 1) is the intensity ratio between the 1.83-eV peak and the 2.02-eV peak. Kuhnke *et al.* found a ratio of about 2, whereas Fig. 1 exhibits a ratio of 15. The reason for this difference is that the spectrum of Kuhnke *et al.* is taken at room temperature while our data were measured at 78 K. The second-harmonic intensity of the resonance at  $\hbar\omega = 1.83$  eV has a much stronger temperature-dependence<sup>6</sup> than the resonance at  $\hbar\omega = 2.02$  eV (Fig. 3).

## B. The nonlinear resonance at 2.3 eV

The fourth resonance in Fig. 1 is at about  $\hbar\omega_1 = 2.3$  eV. In order to be able to measure this resonance it was necessary, as for the case of the 2.02 eV resonance, to perform a SFG experiment with  $\hbar(\omega_1 + \omega_2) \sim 3.7$  eV, i.e., again close to the  $2^1T_{1u}$  state. A SHG experiment in the energy range  $\hbar\omega_1 = 2.12$ –2.38 eV (520–585 nm) yielded no detectable



signal. We assign the resonance at  $\hbar\omega_1 = 2.3$  eV to the excitonic  $^1H_g$  state. This is in agreement with findings from other groups. Wilk *et al.* found indications in their SHG experiments, that the  $^1A_g$  to  $^1H_g$  electric-quadrupole transition is at about 2.33 eV.<sup>12,8</sup> Kuhnke *et al.*<sup>8</sup> observe a peak at  $\hbar\omega = 1.18$  eV in their SHG spectrum, and assign this to the electric-quadrupole transition to the  $^1H_g$  state at  $2\hbar\omega = 2.36$  eV.

The large difference in second-harmonic intensity between the electric-quadrupole transition at 2.3 eV and the magnetic-dipole transition at 1.83 eV was predicted by Koopmans.<sup>3,11</sup> The electric-quadrupole-induced susceptibility should only be 10% of the magnetic-dipole-induced susceptibility, which means that the resonant intensities could be different by as much as two orders of magnitude. Experimentally we find a difference in intensities of about 1.5 orders of magnitude. This discrepancy can be explained as follows.  $C_{60}$  is evaporated on a MgO substrate up to a thickness of about 250 nm. This thickness was chosen to avoid dispersive-interference effects while tuning the fundamental frequency (in  $m \rightarrow p$  polarization combination at  $\hbar\omega = 1.8$  eV). However, since the fundamental frequency had to be tuned over a rather broad range to probe the resonance at  $\hbar\omega = 2.3$  eV, it is likely that the dispersive-interference effect introduces a certain enhancement of the sum-frequency intensity.<sup>27</sup>

### C. Excitons versus interband transitions

Comparing the SHG (SFG) spectrum in Fig. 1 and the SHG spectrum of Kuhnke *et al.*<sup>8</sup> to spectra obtained by one- and two-photon absorption<sup>25,28,29</sup> and electron energy-loss spectroscopy (EELS) in the same energy range<sup>30</sup> one notices the following. In the SHG spectra, the excitons are clearly probed, and there is no visible contribution from the conductivity gap (i.e., interband transitions). In the one-, two-photon absorption and EELS spectra the excitons are observed as well, but are often dominated by the strong contributions from the optically allowed transitions which form the electron-hole continuum.

In an attempt to understand the difference between the SHG and one- and two-photon absorption spectra, one needs to examine the differences between these techniques. The most significant difference is that in one- and two-photon absorption experiments incoherent processes are probed, whereas a SHG experiment involves only coherent processes. This realization has significant implications for our SHG observations. In fact, an exciton is a *charge-neutral* particle, where the electron and hole are bound together, having a single  $\vec{k}$  vector. Since both particles are always bound to each other, and have a common  $\vec{k}$  vector, their probability to recombine without losing their  $\vec{k}$  coherence is much higher than for the case of a free electron and hole, which result from a transition across the conductivity gap. In the latter case the electron and hole are *two charged* particles moving independently through the electron-hole continuum with their own  $\vec{k}$  vector. They are, therefore, far more susceptible to scattering processes and dephasing, i.e., to lose their  $\vec{k}$

coherence, than a bound electron-hole pair. Since in a SHG experiment coherence is a prerequisite, a dephased excitation will not contribute to second-harmonic intensity.

Another clear illustration of the direct relationship between the second-harmonic intensity and the coherency of the probed system during the excitation can be seen from the following: the second-harmonic intensity of the excitonic  $^1T_{1g}$  state in  $C_{60}$  increases strongly close to the rotational-ordering phase transition (at 260 K) down to about 200 K.<sup>6</sup> Since above this phase transition the  $C_{60}$  molecules are rotating uncorrelated, their motion leads to strong ( $T_2$ ) dephasing. It reduces the periodicity and the coherence of the system. Below the phase transition the  $C_{60}$  molecules only alternate between two equilibrium positions. Less dephasing will occur, resulting in an increase in second-harmonic intensity. This enhancement is particularly large, since the second-harmonic intensity is proportional to the square of the number of coherent atoms or molecules involved. Therefore, dephasing processes such as rotations and vibrations of the atoms strongly affect the second-harmonic (or sum-frequency) intensity in a SHG (or SFG) experiment.

At first sight, one might expect that the sum-frequency intensity of the  $C_{60}$  resonance at  $\hbar\omega_1 = 2.02$  eV will exhibit a similar strong temperature-dependent behavior, as the resonance at  $\hbar\omega = 1.83$  eV. However, Fig. 3 shows that this is not the case. By considering the origin of the resonance at  $\hbar\omega_1 = 2.02$  eV, we can comprehend the different temperature dependence of the two resonances. For both resonances the excitonic  $^1T_{1g}$  state is involved. However, for the transition at 2.02 eV a  $t_{1u}$ -phonon mode is included. Due to the coupling to this phonon the excitation still dephases considerably even below the rotational-ordering phase-transition temperature. Below this temperature the temperature dependence of the sum-frequency intensity at  $\hbar\omega_1 = 2.02$  eV will be dominated by the temperature dependence of the phonons rather than the motion of the  $C_{60}$  molecules.

We can now also explain the difference in the SHG spectrum of Kuhnke *et al.*<sup>8</sup> between the second-harmonic intensity of the transition at  $2\hbar\omega = 2.7$  eV and the one at  $\hbar\omega = 2.02$  eV. Both transitions are electric-dipole allowed and single resonant. The transition at  $\hbar\omega = 2.02$  eV involves a phonon and will therefore be less coherent than the purely excitonic transition at  $\hbar\omega = 1.83$  eV. However, it also includes an excitonic state, and it still is a transition below the conductivity gap. On the contrary, the excitation at  $2\hbar\omega = 2.7$  eV (to the  $^1T_{1u}$  state) is above the conductivity gap, implying that it is much more susceptible to scattering processes and dephasing. Hence, it will have much weaker second-harmonic intensity.

We conclude that the SHG measurements show that an exciton exhibits more second-harmonic intensity than an interband transition. To confirm this idea we have studied the Wannier excitons of CuCl in a second-harmonic frequency-dependent experiment.

## IV. WANNIER EXCITONS IN CuCl

In CuCl the energies of the two Wannier excitons, the transverse  $Z_3$  and  $Z_{1,2}$  excitons, are at about 3.203 and 3.271

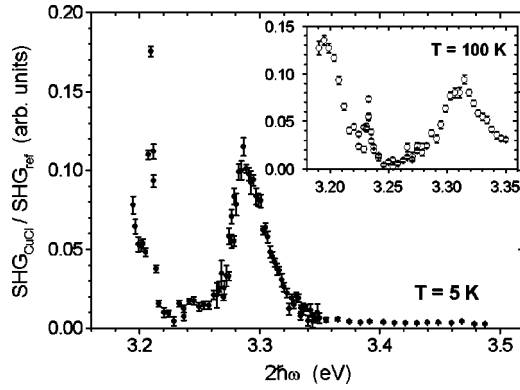


FIG. 4. SHG from a CuCl polycrystalline film measured at 5 K (cryostat temperature, which corresponds to about 25 K for the sample) and at 100 K (see inset). The energy range covers (almost) the two  $1s$  excitons and the conductivity gap of CuCl. The peak at  $\sim 3.3$  eV corresponds to the  $Z_3^T$  exciton and the one at  $\sim 3.2$  eV to the  $Z_{1,2}^T$  exciton. The extremely sharp spike at  $\sim 3.21$  eV is due to accidental phase matching (Ref. 33).

eV, respectively.<sup>15,31</sup> The onset of the conductivity gap is at about 3.40–3.45 eV.<sup>15,17,18,32</sup> In Fig. 4 the result of a SHG experiment covering both energy scales is shown.

At low temperature we clearly see a second-harmonic resonance at 3.287 eV, a sharp peak at 3.21 eV, and the onset of another second-harmonic resonance situated at about 3.18 eV. No enhancement of SHG was detected around the band gap at 3.4 eV. In the inset the 100 K data are shown, confirming that the steep slope around 3.2 eV at 5 K is indeed due to a second-harmonic resonance.

The very sharp peak at 3.21 eV is not due to a second-harmonic resonance. Hauelsen and Mahr<sup>33</sup> observed in their SHG measurements a similar sharp peak at 3.217 eV, i.e., between the two exciton lines. They attributed this spike to an accidental single point of near phase matching ( $\Delta k=0$ ) due to the crossing of the second-harmonic and the fundamental refractive index value, when the second-harmonic photon energy lies between that of the two excitons. Staude<sup>34</sup> calculated the optical constants by a Kramers-Kronig transformation of measured reflectivity data and found that at about 3.217 eV the index of refraction has a value of 1.95. This equals the value of the index of refraction at the fundamental frequency.<sup>35</sup>

That our spike is observed at a slightly lower energy than Hauelsen and Mahr (3.21 eV versus 3.217 eV), can be understood. Our lowest second-harmonic resonance occurs at a somewhat lower energy as well ( $\sim 3.18$  eV versus 3.202 eV). Hence, to first order, the accidental phase matching will also be at a slightly lower energy. This suggests that the optical properties of our CuCl film are slightly different from those of Hauelsen's CuCl crystal. At 100 K, the sharp peak is much less pronounced, which is due to the increasing phonon activity at higher temperatures.

In our SHG measurements the two Wannier excitons,  $Z_3^T$  and  $Z_{1,2}^T$ , are clearly visible, whereas no second-harmonic intensity enhancement was observed above the conductivity gap. On the other hand, in the one-photon absorption<sup>14,15,36</sup>

and two-photon absorption spectroscopic<sup>17,37,38</sup> measurements both the Wannier excitons and the conductivity gap are observed with no particular discrimination. This difference in the probing technique is the same as we already found and discussed for  $C_{60}$ . The SHG data on CuCl support the idea drawn from the  $C_{60}$  SHG and SFG measurements.

## V. CONCLUSIONS

In conclusion, we have performed second-harmonic generation (SHG) and sum-frequency generation (SFG) measurements on  $C_{60}$  and CuCl, in which Frenkel and Wannier excitons were probed, respectively. From these experiments we deduce that excitons can be clearly observed while no contribution from the electron-hole continuum can be found in our spectra. This is very different from spectra obtained by one- and two-photon absorption and EELS. An interpretation of our measurements has been given in terms of the coherence needed for SHG experiments. An interband transition dephases much more rapidly than an exciton, resulting in a strongly reduced SHG signal. With this idea a new understanding of the  $C_{60}$  SHG spectrum of Kuhnke *et al.*<sup>8</sup> is obtained.

It is interesting also to speculate concerning the origin of the SHG and SFG spectra of clean and oxidized Si(100) and Si(111) samples measured by Daum *et al.*<sup>39</sup> They found a strong resonance at  $2\hbar\omega=3.3$  eV, which they assigned to the direct transition between valence- and conduction-band states. With the knowledge deduced from the experimental findings in this paper that excitons will be preferentially seen in a coherent SHG (SFG) experiment (see also Ref. 19), we would like to suggest that this resonance might be due to excitonic states derived from a hole in the  $\Lambda_3$  band and electron in the  $\Lambda_1$  band and a weak coupling between them. The bands have nearly the same dispersion. In linear optics the difference between an excitonic transition and an interband transition between parallel bands is difficult to observe, especially if the excitonic binding energy is only 14.7 meV.<sup>40</sup>

We suggest that a temperature-dependent study of the SHG signal in Si down to low temperature could be used to distinguish between the excitonic or interband transition origin of the signal. If the signal is of excitonic origin, we would expect the SHG signal to strongly increase as the temperature is decreased to values well below the excitonic binding energy of 14.7 meV or 170 K. This is because the dephasing processes due to excitations from the excitonic states to the electron hole continuum would be strongly reduced at temperatures below the exciton binding energy and as we demonstrated in this paper such dephasing processes strongly reduce the SHG intensity while the linear absorption should show a significantly weaker temperature dependence.

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- \*Present address: Philips Research Laboratory, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands. Email: anna-maria.janner@philips.com
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